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THE PROBLEM OF HYDROGEN ISOTOPE EXCHANGE IN  
SATURATED HYDROCARBONS  
(USSR)

[Translation]

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# FOREWORD

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In conducting hydrogen isotope exchange reactions in heavy water, as is well known, the hydrogen atoms in C-H hydrocarbon bonds are either exchanged with great difficulty or practically are not quite changed to deuterium. A. I. Brodskiy [1] figured that it was bonded in the absence of free electron pairs from carbon. A. I. Shatenshteyn and co-workers [2-4] showed, that a hydrogen exchange in C-H bonds is sharply accelerated if the reaction is conducted in such mediums as: deuterioammonia, deuterium bromide or deuterium flouride. However even in such strongly heavy hydrogen mediums, as  $\text{ND}_3$  and  $\text{DBr}$ , hydrogen atoms of saturated hydrocarbons do not exchange.

The problem of hydrogen isotope exchange in saturated hydrocarbons has its own history. Taylor, Morikava and Benedict [5], who succeeded in accomplishing the hydrogen exchange in a gas phase between methane and deuterium by catalyzation with agitated copper atoms, first observed such an exchange in 1935. Later [6] an exchange between methane and ethane on the one hand and atomized deuterium on the other was accomplished. The catalytic action of several metals and oxides on a hydrogen exchange in C-H bonds was studied in a series of works. By this it was shown that the exchange occurs comparatively easily in olefin and aromatic hydrocarbons, whereas in the case of saturated hydrocarbons even in very active catalyzers at high temperature it does not take place or it takes place with great difficulty.

Ingold, Raisin, and Wilson observed the hydrogen exchange of saturated hydrocarbons in heavy hydrogenized sulfuric acid for the first time in 1936 [7]. Later, the exchange of hydrocarbons in deuterio-sulfuric acid was studied in more detail [8-10]. It was pointed out that in the case of hydrocarbons, not containing a tertiary carbon atom, the exchange is not noted, whereas a complete exchange is observed in the presence of even one tertiary C-atom in the molecule. This fact was

explained by the oxidation of the tertiary carbon atom by sulfuric acid with the following exchange in the carbonium ion [9,10] (or olefin [8]), being formed as a result of the oxidation. Since in the exchange process the complete oxidation of hydrocarbon was not observed, the hypothesis was expressed, according to which the carbonium center (or double bond) is transferred both inside the molecule and from one molecule to the other according to the chain mechanism. Thus the presence of a tertiary carbon atom, which may easily be oxidized is acknowledge the necessary condition of an exchange reaction in deuteriosulfuric acid and also the necessity of the very act of oxidation, being the beginning of the chain.

Data [2,11] on the insignificant introduction of deuterium into n-heptane, cyclohexane and decalin molecules by conducting the exchange in a potassium amide solution in liquid heavy hydrogenized ammonia is also available in the literature.

Still in 1951 we studied the hydrogen exchange in cyclohexane in the medium of liquid deuterium bromide in the presence of  $\text{AlBr}_3$ . It was shown, that the exchange reaction in such a medium occurs comparatively easy and in the course of 60 hours at room temperature equilibrium may be attained practically.\* (\* A short reference of the results of these tests were made in the footnote to the article [3] and also in the summary [2].) For greater certainty, besides the tests on the direct exchange, tests on the reverse exchange also were carried out, for which at first cyclohexane was heavy hydrogenized and then dissolved in an  $\text{AlBr}_3$  solution in hydrogen bromide, not containing deuterium, and the introduction of deuterium from cyclohexane into hydrogen bromide was tested.\*\* (\*\* The absence of the isomerization of cyclohexane in methylcyclopentane was checked out in our tests by the invariability of the boiling temperature of cyclohexane  $81.0^\circ\text{C}$ ) up to and after the exchange.)

That case, wherein the hydrogen exchange in saturated hydrocarbons, containing a tertiary carbon atom, must not certainly pass through the oxidation stage, is confirmed by the tests on the isotope exchange in the medium of deuterium fluoride.

Earlier [4] it was shown that such saturated hydrocarbons as methylcyclohexane and decalin, exchange their own hydrogen atoms sufficiently easy in a medium of liquid deuterium fluoride, and in the presence of  $\text{BF}_3$  the exchange may also be successfully observed even in cyclohexane. Tests, which we conducted recently with the application of specially prepared pure deuterium fluoride without oxidizers, confirmed the earlier obtained results [4]. At room temperature in the course of 190 hours 11 hydrogen atoms were exchanged in methylcyclohexane and in the course of 760 hours 13 atoms exchanged.

The obtained results witnessed the fact that  $\text{AlBr}_3$  solutions in hydrogen bromide and also hydrogen flouride and more so  $\text{BF}_3$  solutions in  $\text{HF}^*$  may be used with success in the capacity of a medium for conducting systematic tests of hydrogen isotope exchange in saturated hydrocarbons (\* The acceleration of the hydrogen exchange in hydrocarbons in a medium of deuterium flouride ought to be expected also by the dissolving of such flourides, as  $\text{AsF}_5$  and  $\text{SbF}_5$  [12] in it.)

These results also witness, first, the fact, that an exchange in saturated hydrocarbons must not certainly be accompanied by their oxidation, since hydrogen bromide, hydrogen flouride and also  $\text{AlBr}_3$  and  $\text{BF}_3$  do not possess oxidizing characteristics, and second, the fact, that the presence of a tertiary carbon atom in the molecule is not compulsory for the exchange.

The problem of the mechanism of our observed fast hydrogen exchange in saturated hydrocarbons arouses the principal interest. This is connected with the fact that in saturated hydrocarbons, as is well known, easily polarized  $\pi$ -bonds are lacking, at the expense of which intermediate complexes with proton donors or carbonium ions may be produced comparatively easy. Not excluded was the fact, that our studied exchange reactions pass through the stage of the joining of deuteron to the saturated hydrocarbon molecule from the positively formed charged ion; it is also possible that the process of deuterium introduction in the form of deuteron, and hydrogen loss in the form of a proton occurs in a single act according to the Walden inversion type mechanism. In conclusion we express thanks to the chief of the laboratory, professor A. I. Shatenshteyn for valuable advice.

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